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It is widely known that divalent silver has higher antibacterial performance than monovalent silver. US5, 017, 295 discloses antibacterial agents containing divalent silver. However, such divalent silver will be only kept stable in concentrated acidic environment. As a result, it would be rather difficult and dangerous for the operation, usage, and transportation of such agents.

US5, 089, 275 provides a type of solid antibacterial compound containing divalent silver. This compound is prepared through reacting acidic fluid divalent silver complex with anhydrous calcium sulfate so as to obtain stable hydrated solid. Although the solid antibacterial agents containing divalent silver solves the issue of the liquid state of divalent silver antibacterial agents, the product still faces the deficiency of long term storage stability because divalent silver is not supported onto the solid carriers by ion exchange. Therefore, the field of application is limited due to the fact to its water solubility. i.e. such solid antibacterial agents have to be used in cleaning water, such as swimming pool, bathtub, industry cooling system, and so on.

CN1286915 introduced a kind of inorganic high valence silver phosphate salt antibacterial agent, wherein titanium potassium phosphate salt powder is applied as carrier to be added into silver nitrate water solution so as to enable potassium ions of titanium potassium phosphate to be exchanged with the univalent silver ions to be loaded onto the carrier. Afterwards, filtration, rinse, and calcinations at 1000°C would be followed to obtain solid univalent silver antibacterial agent dispensed into water. And then, potassium persulphate or sodium persulphate would be applied for oxidation purposes, once again, the filtration, rinse and calcinations would be executed for obtaining solid bivalent or trivalent silver antibacterial agents. However, such process was redundant, complicated and costly. Even worse, when solid antibacterial agent containing univalent silver ions are dispensed into water solution to be re-oxidized, certain amount of univalent silver ions would be exchanged by sodium ions. As a result, it is difficult to produce stable high valent silver antibacterial agent based on above mentioned method.

Therefore, it is desirable to make intensified investigate into solid inorganic antibacterial agents containing divalent silver to broaden its field of applications.

What is Claimed is:

1. An inorganic antibacterial agent containing high-valence silver, which are characterized by containing 2 to 6% by weight divalent silver, trivalent silver or tetravalent silver based on total weight of the antibacterial agents, wherein said high-valence silver is supported onto a solid carrier by an ion exchange reaction.
2. The inorganic antibacterial agent containing high-valence silver, as recited in claim 1, wherein said solid carrier is selected from a group consisting of sodium zirconium-phosphate, sodium titanium phosphate, sodium tin phosphate and zeolite.
3. The inorganic antibacterial agent containing high-valence silver, as recited in claim 2, wherein said zeolite is selected from a group consisting of A-type zeolite, X-type zeolite, and Y-type zeolite.
4. The inorganic antibacterial agent containing high-valence silver, as recited in claim 1, further containing 3.7% by weight of said divalent silver, said trivalent silver or said tetravalent silver based on a total weight of said antibacterial agent.
5. The inorganic antibacterial agent containing high-valence silver, as recited in claim 1, wherein an average particle diameter of said inorganic antibacterial agent is ranged from 1.0 – 10.0 μm , preferably 1.0 – 2.0 μm .
6. A method for preparing an inorganic antibacterial agent containing high-valence silver, comprising the following steps:
 - adding a solid carrier, which is capable of ion exchange, into a solution containing high-valence silver;
 - substantially stirring said solution to obtain a pulp formed solution for enabling an ion exchange reaction between said high-valence silver ion and the exchangeable ion of said solid carrier to yield a solid compound, and
 - filtering and drying said solid compound to ultimately obtain said inorganic antibacterial agent containing high valence silver.

7. The method, as recited in claim 6, wherein said solution containing high-valence silver is prepared by dissolving silver peroxide into persulphate or concentrated nitric acid to generate water solution containing bivalent silver, periodic acid solution containing trivalent silver, and silver acid solution containing tetravalent silver.

5 8. The method, as recited in claim 6, wherein said solid carrier is selected from a group consisting of sodium zirconium phosphate, sodium titanium phosphate, sodium tin phosphate and zeolite.

9. The method, as recited in claim 6, wherein a volume ratio between said solid carrier and said solution containing high-valence silver is 1:6-10, preferably 1:8.

10 10. The method, as recited in claim 6, wherein said ion exchange reaction between said high-valence silver and said solid carrier is reacted at a predetermined condition, wherein a pH value is ranged 1-5, preferably 3-5, temperature ranged 30°C to 80°C, preferably 55°C to 65°C, best at 55°C, reacting time ranged 2-8 hours, preferably 4-6 hours, wherein 20% NaOH or KOH is applied for adjusting said pH value.

15 11. The method, as recited in claim 6, wherein said filtering and drying step further comprises sub-steps for washing a filter cake until a pH value ranged between 5-6, preferably 6, and for drying said filter cake at a temperature between 110 °C - 140 °C, preferably at 120 °C for 1 – 2 hours.

20 12. The method, as recited in claim 6, further comprising a step for calcinating said solid compound between 800 °C to 1000 °C, preferable at 900 °C, for 2 – 4 hours, preferable 2 hours, and a step for grinding said solid compound by a gas flow pulverizer to obtain particles with a size of average diameter of 1.0 – 10.0 µm, preferably 1.0 – 2.0 µm.

25 ~~13. comprising antibacterial clothing, antibacterial daily products, antibacterial plastic products, antibacterial medical and mechanical devices, antibacterial structure materials, antibacterial ceramics, antibacterial sanitary ware, and antibacterial home electronic appliances.~~

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的水合固体基质而得以制备。该含二价银的固体杀菌剂虽然解决了上述液体状态的二价银杀菌剂所存在的问题,但在该含二价银的固体杀菌剂中,由于二价银不是通过离子交换而负载在固体载体上,因此,仍然存在着产品长期存放的稳定性问题。并且由于该固体杀菌剂组合物具有水溶性,而使其应用领域受到限制,即,只能用于对泳池、浴盆和工业用冷却装置中的水进行清洁。

CNI286915 提供了一种高价银磷酸盐无机抗菌剂,其通过将作为载体的磷酸钛钾盐粉末加到硝酸银水溶液中,使一价银离子与磷酸钛钾中的钾发生离子交换而负载在磷酸钛钾载体上。然后经过滤、洗涤和在 1000℃ 煅烧处理后,再将获得的一价银固体抗菌剂分散到水中,用过硫酸钾或过硫酸钠进行氧化,并经再次过滤、洗涤和高温煅烧获得含有二或三价银的固体抗菌剂。该方法得到高价银固体抗菌剂的制备过程冗长而复杂、成本高,并且含一价银离子的固体抗菌剂在再次分散到水溶液中进行氧化时,固体载体上的部分一价银会被钠离子交换下来。因此,按照所述方法无法获得具有确定含银量的质量稳定的高价银抗菌剂。

因此,还需要更深入地研究开发含有二价银的固体抗菌剂以使其在更广泛的领域中得以应用。

发明内容

本发明旨在提供一种含高价银的无机抗菌剂,其特征在于,其含有基于抗菌剂总量的 2%重量到 6%重量的二价银、三价银或四价银,所述高价银通过离子交换反应负载在固体载体上。

本发明还提供含高价银的无机抗菌剂的制备方法,该方法包括如下步骤:将可进行离子交换的固体载体加入到所述含高价银的溶液中,所述含高价银的溶液中,二价银离子的浓度为 2-8 %重量,优选为 3.5-5%重量;充分搅拌得到的浆状物以使高价银离子与所述固体载体上的可交换离子发生离子交换反应;过滤并干燥得到的固体产物,得到含高价银的无机抗菌剂。

本发明还进一步提供含高价银的无机抗菌剂在抗菌织物、抗菌日用品、抗菌塑料制品、抗菌医疗用品和器械、抗菌建材、抗菌陶瓷、抗菌洁具和抗菌家电中的应用。

权利要求书

1. 一种含高价银的无机抗菌剂, 其特征在于, 其含有基于抗菌剂总量的 2%重量到6%重量的二价银、三价银或四价银, 所述高价银通过离子交换反应负载在固体载体上。
2. 如权利要求 1 所述的含高价银的无机抗菌剂, 其中所述的固体载体选自: 磷酸铝钠、磷酸钛钠、磷酸锡钠或沸石。
3. 如权利要求 2 所述的含高价银的无机抗菌剂, 其中所述的沸石选自 A 型沸石、X 型沸石或 Y 型沸石。
4. 如权利要求 1 所述的含高价银的无机抗菌剂, 其中含有基于抗菌剂总量的 3.7%重量的二价银、三价银或四价银。
5. 如权利要求 1 所述的含高价银的无机抗菌剂, 其中所述无机抗菌剂的平均粒径为 1.0-10.0 μm , 优选为 1.0-2.0 μm 。
6. 含高价银的无机抗菌剂的制备方法, 该方法包括如下步骤:
将可进行离子交换的固体载体加入到所述含高价银的溶液中;
充分搅拌得到的浆状物以使高价银离子与所述固体载体上的可交换离子发生离子交换反应;
过滤并干燥得到的固体产物, 得到含高价银的固体无机抗菌剂。
7. 如权利要求 6 所述的含高价银的无机抗菌剂的制备方法, 其中所述含高价银的溶液为过氧化银溶解在过硫酸盐或浓硝酸中制成的含二价银的水溶液、含三价银的高碘酸水溶液和含四价银的银酸水

溶液。

8. 如权利要求 6 所述的含高价银的无机抗菌剂的制备方法, 其中所述的固体载体选自: 磷酸锆钠、磷酸钛钠、磷酸锡钠或沸石。

9. 如权利要求 6 所述的含高价银的无机抗菌剂的制备方法, 其中所述的固体载体与所述含高价银的溶液的体积比为 1: 6-10, 优选为 1: 8。

10. 如权利要求 6 所述的含高价银的无机抗菌剂的制备方法, 其中所述固体载体与含高价银之间的离子交换反应在 pH 为 1 到 5, 优选 3 到 3.5, 温度为 30°C-80°C, 优选为 55°C-65°C, 更优选在 55°C 的条件下反应 2-8 小时, 优选 4 到 6 小时, 其中用 20%NaOH 或 KOH 调节反应体系的 pH 值。

11. 如权利要求 6 所述的含高价银的无机抗菌剂的制备方法, 其中所述的过滤干燥步骤包括将滤饼充分水洗至 pH 为 5 到 6, 优选为 6, 并在 110°C 到 140°C, 优选 120°C 干燥 1-2 小时。

12. 如权利要求 11 所述的含高价银的无机抗菌剂的制备方法, 该方法还包括煅烧和粉碎步骤, 其中煅烧温度为 800°C 到 1000°C, 优选为 900°C, 载银磷酸锆煅烧时间为 2-4 小时; 粉碎步骤包括在气流粉碎机中粉碎至平均粒径为 1.0-10.0 μm , 优选为 1.0-2.0 μm 。

13. ~~含高价银的无机抗菌剂在抗菌织物、抗菌日用品、抗菌塑料制品、抗菌医疗用品和器械、抗菌建材、抗菌陶瓷、抗菌洁具和抗菌家电中的应用。~~